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Pressure-Induced 4*f*-5*d* Electron Collapse in Ytterbium Monotelluride

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The pressure-volume relationship in YbTe has been studied by high-pressure x-ray diffraction up to 300 kbar. This relationship is anomalous in the region 150–190 kbar indicating a continuous electronic collapse with pressure, in which the Yb^{2+} changes to Yb^{3+} state. This must involve 4*f*-5*d* electron promotion and must result in a semiconductor-to-metal transition. The behavior of YbTe suggests that in rare-earth chalcogenides with large band gap a continuous transition would be favored.

We report in this paper the occurence of a pressure-induced 4*f*-5*d* electronic collapse in YbTe, in the pressure range 1–190 kbar. Our data suggest that this collapse takes place continuously with pressure rather than abruptly at one pressure. The electronic collapse involves the conversion of Yb^{2+} to Yb^{3+} and is therefore a metal-semiconductor transition.

Recent pressure studies on TmTe,[1] SmTe,[2] SmSe, and SmS[3] have reported that under pressure the rare-earth ions in these compounds undergo a transformation to the trivalent state, without a change in the long-range order (the NaCl-type structure remaining NaCl). Resistivity measurements[2,3] have indicated that this electronic transition involving 4*f*-5*d* electron promotion takes place continuously with pressure in SmTe and SmSe, while in SmS it occurs discontinuously at a pressure of 6.5 kbar. Also, high-pressure x-ray studies[4] have shown that a pressure-induced NaCl → CsCl-type phase transition occurs in PrTe, SmTe, and EuTe.

In ytterbium monochalcogenides, Yb has the full complement of electrons in the 4*f* shell, and their behavior under pressure would be of much interest. We have studied YbTe by high-pressure x-ray diffraction in the range 1 to 300 kbar; in this Letter the results are presented and discussed.

The material was prepared by reacting appropriate amounts of high-purity Yb and Te in a quartz tube at about 700°C and by subsequent melting of the product in a Ta tube kept inside a vacuum chamber. The material thus obtained was polycrystalline with large single-crystal regions. The structure and the lattice constant appropriate to YbTe were verified from x-ray powder patterns of the material. The substance disintegrates to a powdery mass when exposed to air for a length of time. Powdering and handling were therefore done in dry air and in as short a time as possible. The resistivity of the material was in the 10^4-Ω-cm range.

High-pressure x-ray studies were carried out using a diamond-anvil high-pressure x-ray camera of the type described by Bassett, Takahashi, and Stook.[5] Pressure was estimated by using silver as an internal standard.

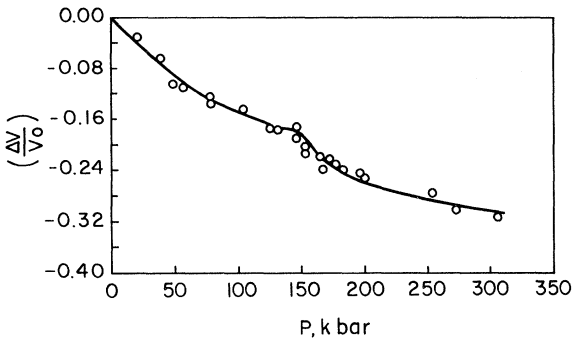

FIG. 1. Pressure-volume relationship for YbTe obtained from lattice-parameter measurements as a function of pressure using the diamond-anvil high-pressure x-ray camera.

Figure 1 shows $\Delta V/V_0$ plotted as a function of pressure. The initial compressibility estimated from the data in the low-pressure range is $K = 0.002$ kbar^{-1}. The compressibility is of the same order as that of EuTe and SmTe. In the 150- to 190-kbar range the compression is anomalous, but there is no change in the structure. The volume change is about 8% in this region. This anomalous compression can only be explained as due to a valence transformation of the Yb ion to the trivalent state. In the trivalent state the Yb ion has a smaller atomic volume compared to Yb^{2+}, and this results in a striking decrease in the lattice constant. The pressure-volume data suggest that this transformation takes place continuously with pressure. In the entire pressure range from 1 to 300 kbar the NaCl-type structure is retained. After the electronic transition YbTe becomes very incompressible.

An isostructural transition involving a large volume change typifies an electronic transition. In YbTe, which is normally a semiconductor, the $4f$ shell is completely full, and in the transition one of the $4f$ electrons is delocalized. The phase transition can be written as $Yb^{2+}Te^{2-} = Yb^{3+}Te^{2-} + 1e$. Thus, one electron per molecule is freed from the localized $4f$ state into the conduction band derived from $6s$-$5d$ states. This should result in a transition from the semiconducting to the metallic state, and one would expect electron transport in the $5d$ band.

A semiconductor-to-metal transition can take place either continuously or discontinuously. The pressure-volume data on YbTe are strongly suggestive of a continuous transition. In this respect YbTe appears to behave like SmTe, and we believe that the gap between the localized $4f$ state and the bottom of the conduction band derived from $6s$-$5d$ states must be shrinking continuously with pressure.

Francillon *et al.*[6] have made resistivity measurements, both under pressure and temperature, on YbTe and have determined the activation energy for carrier activation into the conduction band at various pressures. They obtain a value of -11×10^{-13} eV/kbar for the change in the activation energy with pressure of a donor level lying 0.46 eV below the bottom of the conduction band. It is assumed that this donor level is the $4f$ level of Yb. If this were true one would expect the gap between the $4f$ level and the conduction band to close near about 40 kbar pressure. However, our x-ray data do not support this. It may be that the level lying 0.46 eV below the bottom of the conduction band is associated with an impurity rather than the $4f$ level. Their optical-absorption data show two peaks, one centered at about 2 eV and another near 1.24 eV. Thin-film absorption data on YbTe[7,8] yield a value of about 2.0 eV for the energy gap between the $4f$ level and the crystal-field-split $5d(t_{2g})$ band. If the rate of closure of this gap is taken to be $(-10$ to $-12)\times10^{-3}$ eV/kbar, the merging of the $4f$ level with the $5d$ conduction band at about 200 kbar is consistent with a gap of about 2 eV. Since the compressibility of YbTe is about the same as EuTe and SmTe, it is not unreasonable to assume that the gap between the $4f$ level and the conduction band in YbTe decreases with pressure at about the same rate as the latter two. Above 200 kbar the Yb ions would all be in the trivalent state. On the basis of a simple model involving a localized state and a conduction-band state whose energy separation is shrinking with pressure, the fractional conversion would be given by

$$Yb^{3+}/Yb^{2+}(P) \approx \{\exp[\Delta E_g(P)/kT] - 1\}^{-1},$$

where $\Delta E_g(P)$ is the pressure-dependent energy separation between the $4f$ level and the $5d$ conduction band. It can easily be seen from this that the conversion of Yb^{2+} to Yb^{3+} would make a contribution to the change in the lattice constant only near pressures where the gap is approaching zero. The pressure-volume relationship reproduced in Fig. 1 is not inconsistent with this model and strongly suggests that a continuous electronic transition takes place with pressure, as the gap between the localized $4f$ level and the conduction band decreases with pressure.

Falicov and Kimball[9] have proposed a model

for the metal-semiconductor transition, which involves a localized state and a conduction-band state whose energy separation decreases with temperature or pressure. They define an effective energy gap given by the equation $\Delta_{eff} = \Delta - 2Gn$, where Δ is the energy gap at $T = 0$ and $P = 0$, G is the strength of electron-hole interaction, and n is the number density of electrons excited into the conduction band. According to this model the number n of electrons in the conduction band can vary continuously or discontinuously with temperature at $P = 0$, depending on the relative values of G and Δ. Bucher[10] has recently extended these ideas and has shown that the model can lead to first- and second-order electronic phase transitions at $T = 0$ when pressure is varied. The parameter G, which is a measure of the strength of electron-hole interaction, has to exceed a certain critical value compared to the total band energy, in order to get a first-order transition under pressure. YbTe has a gap of about 2 eV, and apparently in materials with large gap the ratio G/Δ is below the critical value for a discontinuous transition.

Europium telluride also has a gap of about 2 eV, and Rooymans[11,12] reported a discontinuous electronic phase transition involving the conversion of an Eu ion to the trivalent state near 30 kbar. However, our p-V data[4] on EuTe up to 100 kbar do not show any evidence of an electronic transition. Near 100 kbar the NaCl-type structure transforms to the CsCl structure.[4] Hence, it appears from the behavior of YbTe that if the energy gap is large, a continuous electronic transition would be favored in the rare-earth chalcogenides.

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Properties of the Interstitial in the Diamond-Type Lattice

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Linear combination of atomic orbital–molecular orbital cluster calculations using extended Hückel theory suggest that the interstitial carbon atom in diamond prefers an "interstitialcy" configuration. The predicted minimum-energy configuration changes with charge state, providing a possible example of the Bourgoin mechanism for "athermal" migration of the interstitial in the presence of ionizing radiation.

Considerable interest and mystery surround the properties of an interstitial host atom in the diamond-type lattice. This fundamental defect must be formed, for instance, as the Frenkel partner to the lattice vacancy in a radiation-damage experiment. In silicon, lattice vacancies produced in such experiments have been detected directly by EPR.[1-3] However, the interstitials